REMARKS

Status of the Application

In the Office Action, claims 1-39 were rejected. In the present response, no claims have been amended, added or deleted so that claims 1-34 are pending. No new matter has been added.

Rejections Under 35 U.S.C. § 103(a)

Claims 1-39 stand rejected under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 5,403,912 to Gunatillake. The Examiner asserts that "it would have been obvious to one of ordinary skill in the art to select ethylene glycol (C2) to replace decane diol (C10) and to select the steps of the processes from the reference within the limitation of the instant claims to form the claimed product, a poly(trimethylene ethylene ether) diol, since they have been shown to be effective in a similar system and thus would have been expected to provide adequate results." The Examiner further assert that "[t]here is no showing of unexpected results derived from said selection."

Specifically, the Examiner asserts that the abstract and column 2, line 4 et seq. of Gunatillake "discloses processes for the production of poly(alkylene oxide) which includes providing a polyhydroxy compound or compounds and an acid resin catalyst or a salt thereof that has been converted to the acid form; and reacting said polyhydroxy compound or compounds in the presence of said acid resin catalyst at a temperature and under conditions to allow polymerization". The Examiner also asserts that "at least in Example 9 at col. 6, the reference discloses a mixture of two diols such as 1,3-propanediol and a decanediol under conditions to form a poly(trimethylene decane ether) glycol."

The Examiner admits that the "disclosure of the reference differs from the instant claims in that it does not disclose the condensation product of 1,3-propanediol and ethylene glycol reactants nor the steps of the continuous, semi-continuous and batch processes to form the product." The Examiner, however, claims that "at least one Example discloses the condensation product of 1,3-propanediol and a decane diol to form the copolymer, as stated above." The Examiner further asserts that "polyhydroxy compounds including alkanediols having from 2 to 20 carbon atoms" are disclosed at column 3, lines 25-30 of Gunatillake,

and that Gunatillake further discloses "the use of [] very broad teachings of steps under conditions to form the products."

Applicants, however, respectfully assert that a person of ordinary skill in the art would not have expected an ethylene glycol and 1,3-propanediol to be capable of being copolymerized in the presence of an acid catalyst to a linear copolymer. In contrast, a person of ordinary skill in the art would have expected the ethylene glycol to cyclize in the presence of acid catalyst, and the 1,3-propanediol to be polymerized to a homopolymer.

In fact, it is well known to a person of ordinary skill in the art that ethylene glycol cannot be polymerized to a homopolymer in the presence of an acid catalyst because the ethylene glycol dimerizes first to diethylene glycol and subsequently the diethylene glycol cyclizes to 1,4-dioxane. Indeed, Applicants direct the Examiner's attention to pages 695-700 of the Encyclopedia of Chemical Technology, Kirk-Othmer, Vol. 12, 4th Ed., John Wiley & Sons, Inc. (1994), which is attached hereto as Exhibit A. More specifically, Applicants direct the Examiner's attention to page 699, wherein Exhibit A expressly indicates that "[d]iethylene glycol readily dehydrates using an acid catalyst to make 1,4-dioxane", and that "[e]thylene glycol also produces 1,4-dioxane by acid-catalyzed dehydration to diethylene glycol followed by cyclization." As evidenced by Exhibit A, Applicants respectfully assert that a person of ordinary skill in the art would know that an ethylene glycol cannot be polymerized to a homopolymer in the presence of an acid catalyst, but rather forms a diethylene glycol and then cyclizes to 1,4-dioxane in the presence of acid catalyst.

In light of such knowledge, a person of ordinary skill in the art would NOT have expected an ethylene glycol to be successfully copolymerized with a 1,3-propanediol so as to successfully produce a linear copolymer in accordance with Applicants' claimed invention. Instead, a person of ordinary skill in the art would have expected the ethylene glycol to cyclize and the 1,3-propanediol to polymerize to a homopolymer in the presence of an acid catalyst.

Applicants further direct the Examiner's attention to Example 8, wherein Applicants unsuccessfully attempted to copolymerize 1,3-propanediol and diethylene glycol in the presence of sulfuric acid catalyst. As the Examiner will note, the reaction mixture turned dark brown and the experimental run had to be stopped. Applicants discovered by the refractive index of the distillate that cyclic dioxane was

present in the distillate. Applicants respectfully assert, that a person of ordinary skill in the art would have expected the same result with ethylene glycol. Indeed, a person of ordinary skill in the art would have expected an attempt to copolymerize ethylene glycol and 1,3-propanediol in the presence of an acid catalyst to be unsuccessful, wherein instead of a copolymer of 1,3-propanediol and ethylene glycol being formed, the ethylene glycol would instead cyclize into a cyclic dioxane.
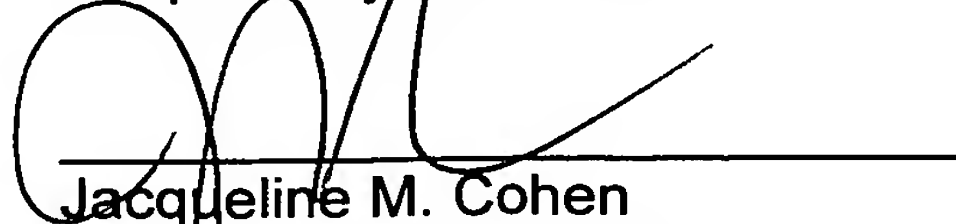
Applicants, however, have unexpectedly discovered that ethylene glycol and 1,3-propanediol can be successfully polymerized to a linear copolymer in the presence of an acid catalyst. Applicants respectfully assert that while Gunatillake generally discloses that polyhydroxy compounds having 2 to 20 carbon atoms can be dehydrated in the presence of a sulfonic acid to form oligomers and co-oligomers, a person of ordinary skill in the art would not have expected such disclosure to encompass an ethylene glycol compound. Rather, as already pointed out hereinabove, a person of ordinary skill in the art would have expected the ethylene glycol to cyclize in the presence of the acid catalyst just like the diethylene glycol of Applicants' Example 8.

As a result, Applicants respectfully assert that ethylene glycol and 1,3-propanediol were unexpectedly found to copolymerize to a linear copolymer in the presence of an acid catalyst, and therefore respectfully request that the Examiner withdraw this rejection.

SUMMARY

In view of the foregoing remarks, Applicants respectfully submit that the application is in condition for allowance. In order to expedite disposition of this case, the Examiner is invited to contact Applicants' representative at the telephone number below to resolve any remaining issues. Should there be a fee due that is unaccounted for, please charge such fee to Deposit Account No. 04-1928 (E.I. du Pont de Nemours and Company).

Respectfully Submitted,

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DATED: August 19, 2004   Facsimile: (302) 658-1192

Kirk-Othmer
Encyclopedia of Chemical Technology
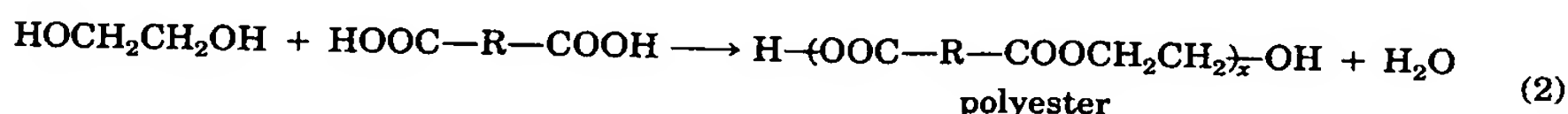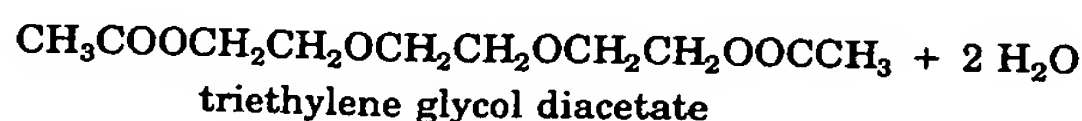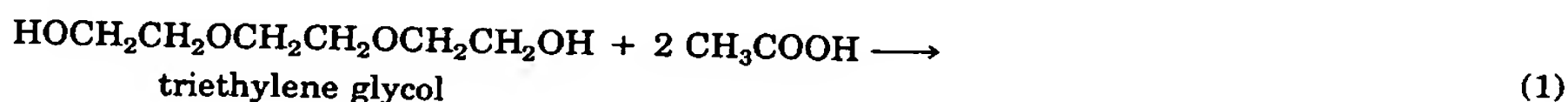
ENCYCLOPEDIA OF

CHEMICAL

GLYCOLS

ETHYLENE GLYCOL AND OLIGOMERS

Glycols are diols, compounds containing two hydroxyl groups attached to separate carbon atoms in an aliphatic chain. Although glycols may contain heteroatoms, those discussed here are composed solely of carbon, hydrogen, and oxygen. These are adducts of ethylene oxide and can be represented by the general formula, $C_{2n}H_{4n}O_{n-1}(OH)_2$.

Ethylene glycol, the adduct of water and ethylene oxide, is the simplest glycol and is the principal topic of this article. Diethylene, triethylene, and tetraethylene glycols are oligomers of ethylene glycol. Polyglycols are higher molecular weight adducts of ethylene oxide and are distinguished by intervening ether linkages in the hydrocarbon chain. These polyglycols are commercially important; their properties are significantly affected by molecular weight. They are water soluble, hygroscopic, and undergo reactions common to the lower weight glycols (see also POLYETHERS, ETHYLENE OXIDE POLYMERS).

Ethylene glycol, EG, is a colorless, practically odorless, low viscosity, hygroscopic liquid of low volatility. It is completely miscible with water and many organic liquids. EG was first prepared by Wurtz in 1859 by hydrolysis of ethylene glycol diacetate. It did not achieve commercial interest until World War I, when it was used in Germany as a substitute for glycerol (qv) in explosives manufacture (1). The uses for ethylene glycol are numerous. Some of the applications are polyester resins for fiber, PET containers, and film applications; all-weather automotive antifreeze and coolants, defrosting and deicing aircraft; heat-transfer solutions for coolants for gas compressors, heating, ventilating, and air-conditioning systems; water-based formulations such as adhesives, latex paints, and asphalt emulsions; manufacture of capacitors; and unsaturated polyester resins. The oligomers also have excellent water solubility but are less hygroscopic and have somewhat different solvent properties. The number of repeating ether linkages controls the influence of the hydroxyl groups on the physical properties of a particular glycol.

Glycols undergo reactions common to monohydric alcohols forming esters, acetals, ethers, and similar products. For example, both simple and polyesters are produced by reaction with mono- or dibasic acids (eqs. 1 and 2):

$$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH + 2\ CH_3COOH \longrightarrow$$

triethylene glycol

(1)

$$CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2OOCCH_3 + 2\ H_2O$$

triethylene glycol diacetate

$$HOCH_2CH_2OH + HOOC-R-COOH \longrightarrow H\text{-}(OOC-R-COOCH_2CH_2)_x\text{-}OH + H_2O$$

polyester

(2)

Physical Properties

Ethylene glycol and its lower polyglycols are colorless, odorless, high boiling, hygroscopic liquids completely miscible with water and many organic liquids. Physical properties of ethylene glycols are listed in Table 1. Vapor-pressure curves of the ethylene glycols at various temperatures are illustrated in Figure 1. Ethylene glycols markedly reduce the freezing point of water (Fig. 2). Some important physical constants of ethylene glycol are given in Table 2.
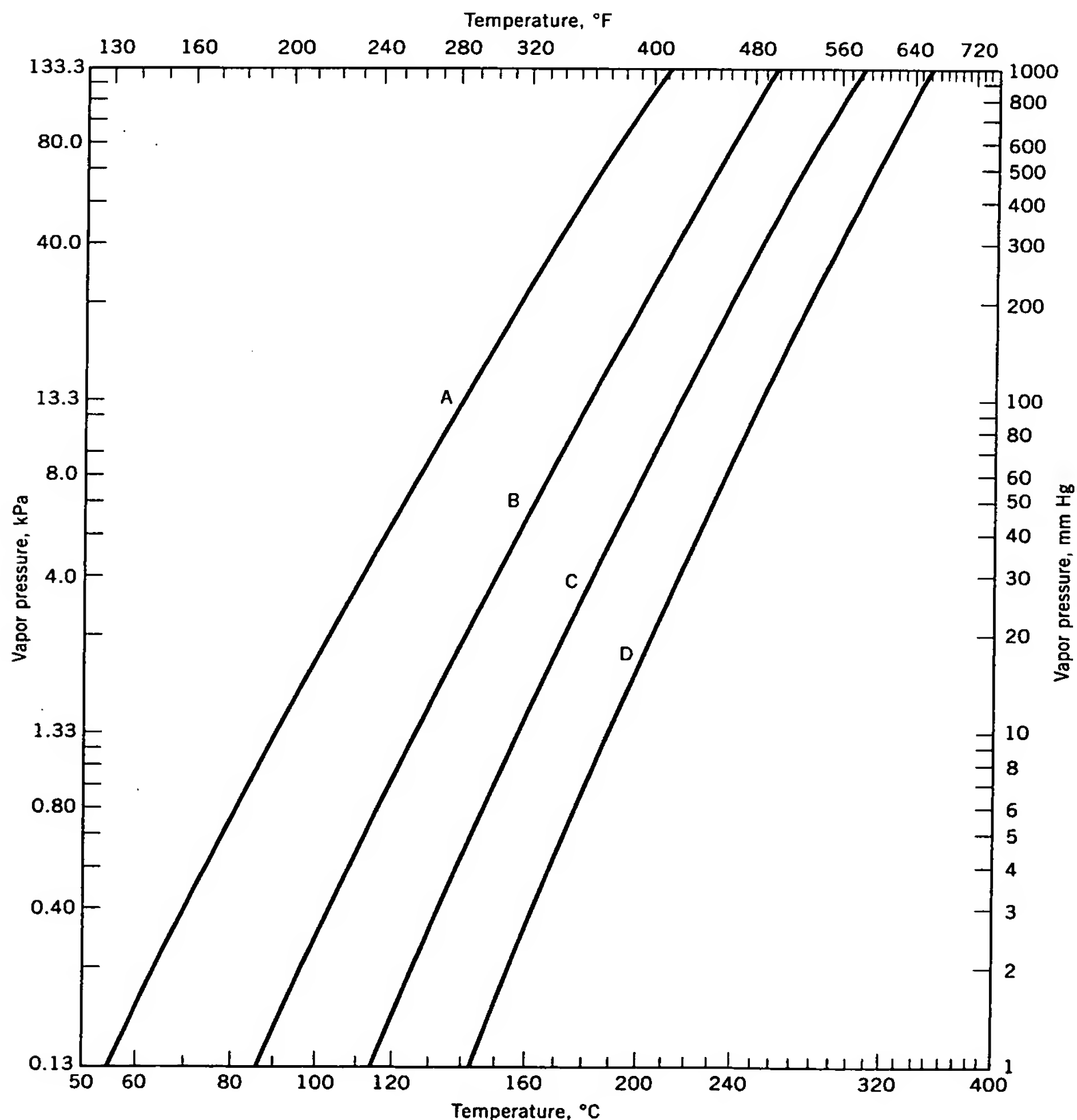

Fig. 1. Vapor pressures of glycols at various temperatures. A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; and D, tetraethylene glycol.

Vol. 12

Table 1

Property

CAS Reg
formula
mol wt
sp gr, 20
bp at 10
mp, °C
viscosity
  mPa·s
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Table 1. Properties of Glycols[a]

Property	Ethylene glycol	Diethylene glycol	Triethylene glycol	Tetraethylene glycol
CAS Registry Number	[107-21-1]	[111-46-6]	[112-27-6]	[112-60-7]
formula	$HOCH_2CH_2OH$	$HO(CH_2CH_2O)_2H$	$HO(CH_2CH_2O)_3H$	$HO(CH_2CH_2O)_4H$
mol wt	62.07	106.12	150.17	194.23
sp gr, 20/20°C	1.1155	1.1185	1.1255	1.1247
bp at 101.3 kPa,[b] °C	197.6	245.8	288	dec
mp, °C	− 13.0	− 6.5	− 4.3	− 4.1
viscosity at 20°C, mPa·s($=$cP)	20.9	36	49	61.9
refractive index, n_D^{20}	1.4318	1.4475	1.4561	1.4598
heat of vaporization at 101.3 kPa,[b] kJ/mol[c]	52.24	52.26	61.04	62.63
flash point of commercial material, °C	116[d]	138[e]	172[e]	191[e]

[a]Ref. 2–5.
[b]To convert kPa to mm Hg, multiply by 7.5.
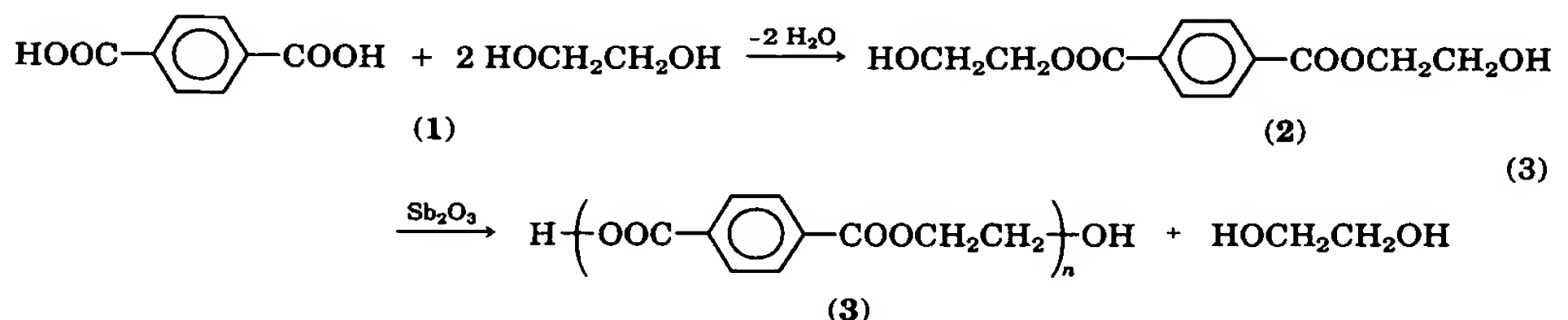[c]To convert kJ to kcal, divide by 4.184.
[d]Determined by ASTM D56, using the Tag closed cup.
[e]Determined by ASTM D92, using the Pensky-Martens closed cup.

Chemical Properties

The hydroxyl groups on glycols undergo the usual alcohol chemistry giving a wide variety of possible derivatives. Hydroxyls can be converted to aldehydes, alkyl halides, amides, amines, azides, carboxylic acids, ethers, mercaptans, nitrate esters, nitriles, nitrite esters, organic esters, peroxides, phosphate esters, and sulfate esters (6,7).

The largest commercial use of ethylene glycol is its reaction with dicarboxylic acids to form linear polyesters. Poly(ethylene terephthalate) [25038-59-9] (PET) is produced by esterification of terephthalic acid [100-21-0] (1) to form bishydroxyethyl terephthalate [959-26-2] (BHET) (2). BHET polymerizes in a transesterification reaction catalyzed by antimony oxide to form PET (3).

$$HOOC-\bigcirc-COOH \ + \ 2 \ HOCH_2CH_2OH \ \xrightarrow{-2 \ H_2O} \ HOCH_2CH_2OOC-\bigcirc-COOCH_2CH_2OH$$

(1)   (2)

(3)

$$\xrightarrow{Sb_2O_3} \ H \left(OOC-\bigcirc-COOCH_2CH_2 \right)_n OH \ + \ HOCH_2CH_2OH$$

(3)

Ethylene glycol esterification of BHET is driven to completion by heating and removal of the water formed. PET is also formed using the same chemistry start-
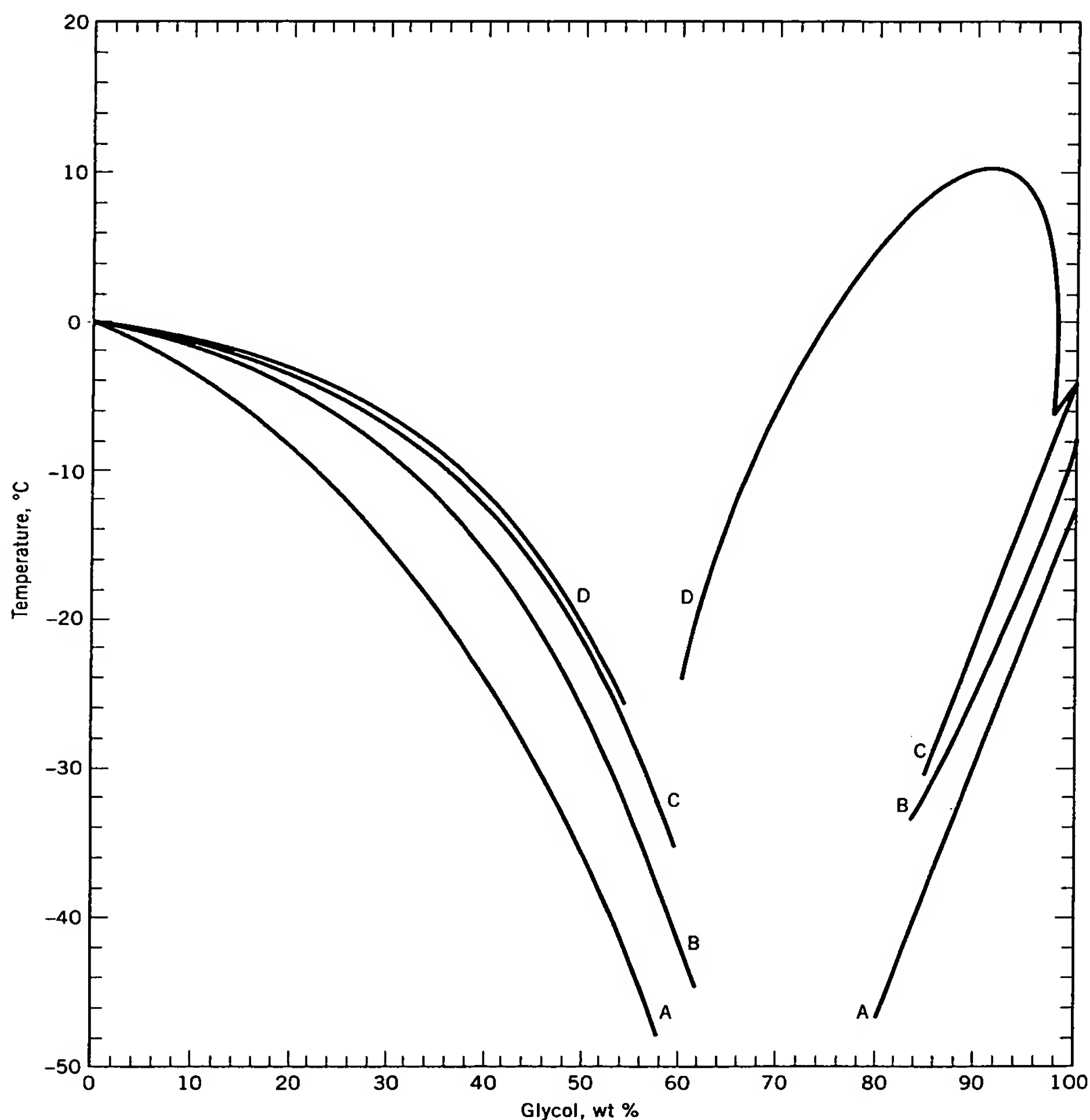
Vapor pressure, mm Hg (scale on left margin): 1000, 800, 600, 500, 400, 300, 200, 100, 80, 60, 50, 40, 30, 20, 10, 8, 6, 5, 4, 3, 2, 1

Fig. 2. Freezing points of aqueous glycol solutions. A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; and D, tetraethylene glycol. Ethylene glycols form a slush with water in the apparent discontinuous ranges.
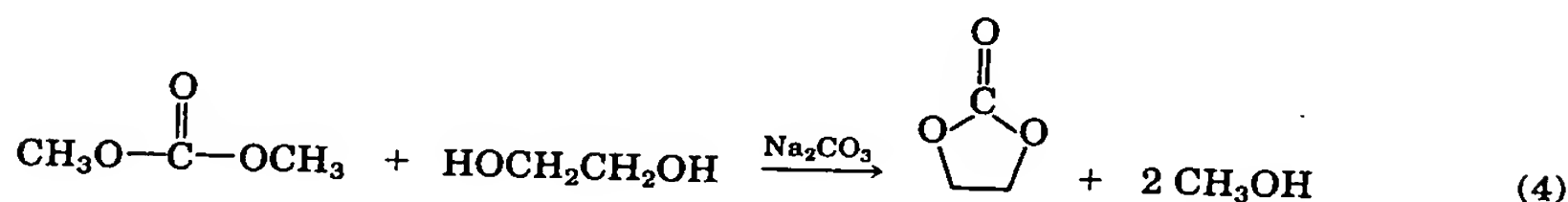
Dieth
[*123-9*

ing with dimethyl terephthalate [*120-61-6*] and ethylene glycol to form BHET also using an antimony oxide catalyst.

Glycols may undergo intramolecular cyclization or cyclically condense with other molecules to form a number of ring structures. Transesterification of carbonates with ethylene glycol produces ethylene carbonate [*96-49-1*] (eq. 4). Numerous materials catalyze carbonate transesterifications.
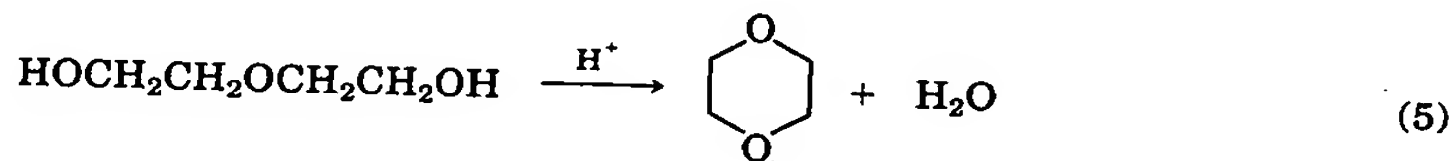
Ethyl
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subse

Table 2. Physical Properties of Ethylene Glycol[a]

Property	Value
flash point	
Pensky-Martens closed cup, °C	127
Cleveland open cup, °C	127
autoignition temperature, °C	400
density at 20°C, g/mL	1.1135
surface tension at 20°C, mN/m(=dyn/cm)	48.4
specific heat, J/(g·K)[b]	
as liquid, 19.8°C	2.406
as ideal gas, 25°C	1.565
electrical conductivity at 20°C, S/m	1.07×10^{-4}
solubility in water at 20°C, % by wt	100.0
solubility of water in EG at 20°C, % by wt	100.0
heat of combustion at 25°C, kJ/mol[b]	−1189.595
heat of formation at 25°C, kJ/mol[b]	−392.878
heat of fusion, kJ/mol[b]	11.63
onset of initial decomposition, °C	165
critical constants	
temperature, °C	446.55
pressure, kPa[c]	6515.73
volume, L/mol	0.186
compression factor, Z_c	0.2671
viscosity, mPa·s(=cP)	
at 0°C	51.37
at 40°C	9.20

[a]Ref. 2; see also Table 1.
[b]To convert J to cal, divide by 4.184.
[c]To convert kPa to mm Hg, multiply by 7.5.

$$CH_3O-\overset{O}{\underset{\|}{C}}-OCH_3 \ + \ HOCH_2CH_2OH \xrightarrow{Na_2CO_3} \quad + \ 2\,CH_3OH \qquad (4)$$

Diethylene glycol readily dehydrates using an acid catalyst to make 1,4-dioxane [123-91-1] (eq. 5).

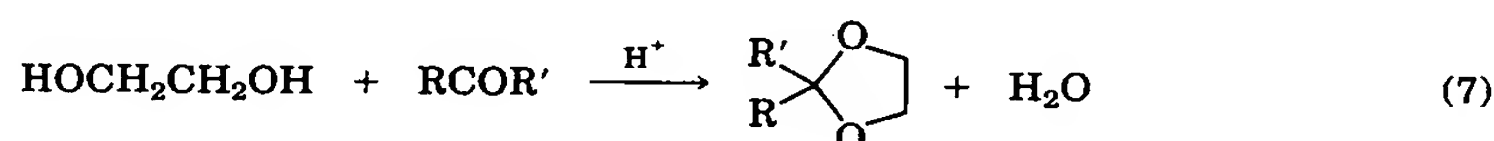$$HOCH_2CH_2OCH_2CH_2OH \xrightarrow{H^+} \quad + \ H_2O \qquad (5)$$

Ethylene glycol also produces 1,4-dioxane by acid-catalyzed dehydration to diethylene glycol followed by cyclization. Cleavage of triethylene and higher glycols with strong acids also produces 1,4-dioxane by catalyzed ether hydrolysis with subsequent cyclization of the diethylene glycol fragment. Diethylene glycol con-

denses with primary amines to form cyclic structures (eq. 6), eg, methylamine [74-89-5] reacts with diethylene glycol to produce N-methylmorpholine [109-02-4].

$$HOCH_2CH_2OCH_2CH_2OH \ + \ CH_3NH_2 \ \longrightarrow \ O\!\!\bigcirc\!\!N\!\!-\!\!CH_3 \ + \ 2\,H_2O \qquad (6)$$

Ketones and aldehydes react with ethylene glycol under acidic conditions to form 1,3-dioxolanes (cyclic ketals and acetals) (eq. 7).

$$HOCH_2CH_2OH \ + \ RCOR' \ \xrightarrow{H^+} \ \underset{R}{\overset{R'}{>}}\!\!\!\!<\!\!\overset{O}{\underset{O}{\bigg]}} \ + \ H_2O \qquad (7)$$
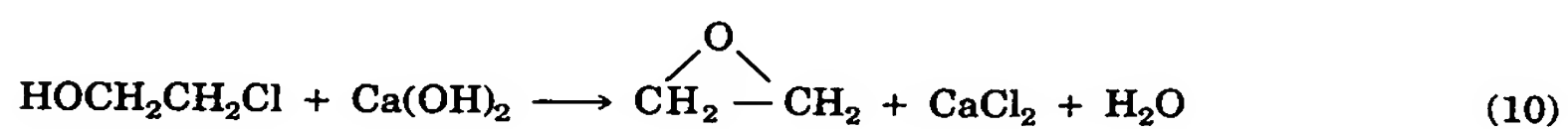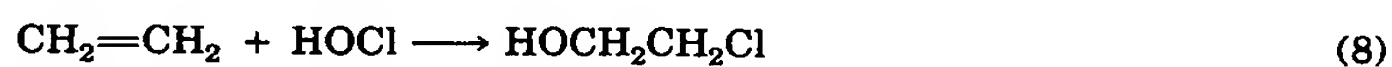
Manufacture

In 1937 the first commercial application of the Lefort direct ethylene oxidation to ethylene oxide [75-21-8] followed by hydrolysis of ethylene oxide became, and remains in the 1990s, the main commercial source of ethylene glycol production (1) (see ETHYLENE OXIDE). Ethylene oxide hydrolysis proceeds with either acid or base catalysis or uncatalyzed in neutral medium. Acid-catalyzed hydrolysis activates the ethylene oxide by protonation for the reaction with water. Base-catalyzed hydrolysis results in considerably lower selectivity to ethylene glycol. The yield of higher glycol products is substantially increased since anions of the first reaction products effectively compete with hydroxide ion for ethylene oxide. Neutral hydrolysis (pH 6–10), conducted in the presence of a large excess of water at high temperatures and pressures, increases the selectivity of ethylene glycol to 89–91%. In all these ethylene oxide hydrolysis processes the principal by-product is diethylene glycol. The higher glycols, ie, triethylene and tetraethylene glycols, account for the remainder.

The large excess of water from the hydrolysis is removed in a series of multiple-effect evaporators (8), and the ethylene glycol is refined by vacuum distillation. Figure 3 depicts a typical process flow diagram.

Ethylene glycol was originally commercially produced in the United States from ethylene chlorohydrin [107-07-3], which was manufactured from ethylene and hypochlorous acid (eq. 8) (see CHLOROHYDRINS). Chlorohydrin can be converted directly to ethylene glycol by hydrolysis with a base, generally caustic or caustic/bicarbonate mix (eq. 9). An alternative production method is converting chlorohydrin to ethylene oxide (eq. 10) with subsequent hydrolysis (eq. 11).

$$CH_2\!\!=\!\!CH_2 \ + \ HOCl \longrightarrow HOCH_2CH_2Cl \qquad (8)$$

$$HOCH_2CH_2Cl \ + \ NaOH \longrightarrow HOCH_2CH_2OH \ + \ NaCl \qquad (9)$$

$$HOCH_2CH_2Cl \ + \ Ca(OH)_2 \longrightarrow CH_2\overset{O}{\overset{\triangle}{-}}CH_2 \ + \ CaCl_2 \ + \ H_2O \qquad (10)$$